

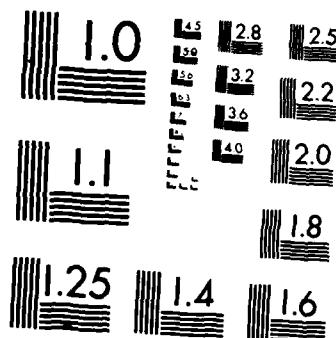
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SURFACE SCIENCE AND TECHNOLOGY M GRUNZE ET AL

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TECHNICAL REPORT NO. 1

Preparation and Adhesion of Ultra Thin Polyimide
Films on Polycrystalline Silver

by

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Prepared for publication in Chem. Phys. Lett.

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Preparation and Adhesion of Ultra-Thin Polyimide Films

on Polycrystalline Silver

by

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Abstract

We deposited 4,4-Oxydianiline (ODA) and 1,2,3,5 Benzenetetracarboxylic Anhydride (PMDA) from the vapor phase onto a polycrystalline silver substrate and followed the polymerization of the two components to form ultra-thin polyimide films ($d \approx 11\text{\AA}$) by X-ray photoelectron spectroscopy. Both PMDA and ODA chemisorb on the clean surface under partial fragmentation. Co-deposition of ODA and PMDA followed by heating of the substrate led to formation of thermally stable ($T < 450^\circ\text{C}$) polyimide films. Our data indicate that adhesion of the polyimide film to the surface involves chemical bonding to fragmented PMDA and/or ODA chemisorbed on the substrate. Our experiments show that polyimide films can be prepared sufficiently thin to allow the application of surface sensitive techniques to probe the substrate-polymer interface and to study the basic physics and chemistry of adhesion.

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Polyimides are used widely in electronic devices as dielectrics or as α -particle barriers in charge sensitive memory devices. Their favorable mechanical and dielectric properties, their thermal stability as well as their ease of application by spin coating favors their use over other polymers. However, their adhesive properties on various substrates are not well understood. There exists no direct information about the polymer film-substrate interaction, i.e. whether adhesion of the film is caused by covalent bonds, electrostatic or dispersive forces, or by mechanical interlinking of the polymer and substrate. Experiments on the nature of polyimide adhesion to metals so far have been restricted to the study of metal clusters and metal films deposited on cured polyimide surfaces or polyimide compounds /1,2/. These experiments showed that different metals interact differently with the polymer surface, e.g. chromium seems to bond covalently with the PMDA section of the polymer through fracturing of the carbonyl bonds, whereas the interaction with copper atoms seems to be restricted to a weak interaction with the oxygen in the ODA-part of the polymer chains. However, the bonding of polyimide films on solid metal surfaces could be considerably different because of the different electronic and therefore chemical properties of bulk metals as compared to clusters or single metal atoms. In this report, we describe the first data on the adsorption of ODA and PMDA on a metal surface and demonstrate that ultra-thin polyimide films can be produced by vapor phase deposition of the two polymer constituents to provide model systems for studying the chemistry of adhesion at a molecular level.

Solventless polyimide film preparation by vapor deposition was first demonstrated for relatively thick ($> 1\mu\text{m}$) films by Salem et al. /3/ using a vapor deposition system. In their experiments, both ODA and PMDA vapors produced by sublimation of the bulk components were mixed in a vapor mixing chamber and then deposited onto the substrate. Our experiments were performed in a Leybold Heraeus XPS system equipped with an ultra high vacuum preparation chamber and a high pressure reactor. Deposition of the ODA and PMDA films was carried out in the preparation chamber. ODA and PMDA of 99% purity (Aldrich Chemical Company) were contained in quartz tubes (50mm length, 5mm diameter) mounted on a 35mm flange and were heated by thermal conduction from a resistively heated tungsten wire. Thermocouples pressed into the materials were used to measure the sublimation temperatures. It was found that the best results for deposition of ODA and PMDA were obtained at sublimation temperatures of $100^\circ - 200^\circ\text{C}$ resulting in ODA and PMDA background pressures in the preparation chamber of $2 \times 10^{-6} - 3 \times 10^{-6}\text{ mbar}$.

No attempts were made to calibrate the evaporation fluxes in these experiments. Prior to deposition, the materials were degassed at the sublimation temperature for 30 min. before the sample was moved into the preparation chamber. The silver substrate was maintained at room temperature during vapor deposition and was cleaned prior to film deposition by oxidation in 0.5mbar of O_2 at 400°C to remove residual carbon and subsequent flashing to high temperatures, or by Ar-ion bombardment.

The spectra reproduced here were recorded with $MgK\alpha$ radiation (100W) and with an experimental resolution of 0.92eV. The electron binding energies given are calibrated against the $Au\ 4f_{5/2}$ emission at $E_B = 84\text{eV}$. The film thickness was estimated from the attenuation of the Ag 3d photoemission signal assuming a homogeneous overlayer and using an electron mean free path of $12\text{\AA}/4$ for the Ag 3d electron through the organic overlayers. The values for the average film thickness can only be considered to be approximate and most likely underestimate the true thickness. For the very thin films ($d \sim 11\text{\AA}$) the intensity of the low kinetic energy silver Auger transition at 351eV indicates that the film is not continuous.

Fig. 1 shows schematically the reaction between ODA (Oxydianiline) and PMDA (Pyromellitic dianhydride or 1,2,3,5 Benzenetetracarboxylic Anhydride) to form polyimide /5/. Initial interaction leads to the formation of the polyimide precursor, i.e. polyamic acid. Heating to $T \geq 120^\circ\text{C}$ eliminates the hydroxyl groups and formation (imidization) of polyimide is observed. The numbers in the structural formulae are given to facilitate an assignment of our X-ray photoelectron spectra to specific carbon atoms in the reactants, intermediates and the product.

In Fig. 2 the carbon 1s spectra and the N 1s spectra of the vapor deposited pure reactants, of a co-deposited layer, and the final polymers are displayed. Spectrum 2a shows the C 1s data for a thin (i.e. monolayer or less) deposit of PMDA. Calibration spectra of bulk PMDA and thick PMDA films /6/ show a doubled C 1s spectrum arising from the aromatic phenyl carbons (1) and the carbonyl carbons (2) with an expected intensity ratio of $R = 6:4$. The spectrum (2a) of the thin PMDA vapor deposited film however, shows a split carbonyl band with two major components ($E_B = 289.6\text{eV}$ and $E_B = 288.4\text{eV}$) indicating a chemical interaction with the substrate. The split carbonyl band exists up to completion of a monolayer. The integrated intensity ratio between the phenyl carbon 1s band at 285.7eV and the carbonyl C 1s bands is $R = (6 \pm 0.3):3$. This ratio is independent on the electron emission angle (90° to 40°) which indicates that the reason for the deviation from the expected intensity ratio is not attenuation of carbon 1s electrons.

Since in undissociated PMDA the ratio of the phenyl carbon to the carbonyl carbon is 6:4, we conclude that one carbonyl group is lost from the surface upon initial deposition. This conclusion is supported further by the phenyl C 1s to O 1s (PMDA: R = 6:6) and carbonyl C 1s to O 1s (PMDA: R = 4:6) signal intensity ratio of R = 6:5 and R = 3:5, respectively /6/.

The comparison of the intensity ratios can help to identify the stoichiometry of the adsorbate phase, but does not indicate the total degree of dissociation of those species or fragments remaining on the surface. The energy separation of the phenyl and carbonyl 1s bands in PMDA is 3.7eV (see spectrum 2b) and it appears that some of the carbonyls in spectrum 2a remain in the same chemical environment as in undissociated PMDA. This observation is suggestive of a bonding configuration of partly dissociated PMDA, where the plane of the molecule is tilted away from the surface and chemical bonding occurs via the carbon atom on the phenyl ring from which CO was released and/or the oxygen on the carboxyl group /6/. Further evaporation of PMDA leads to the formation of an undissociated PMDA film on top of the partly dissociated layer as shown in spectrum 2b. The shift of the C1s bands to higher binding energies is explained by a decrease in final state screening of the photoionized molecule by metal electrons in the thicker films.

Spectrum 2c was recorded from an oxydianiline film of $d \sim 17\text{\AA}$. The major band at $E_B = 285.6\text{eV}$ originates from the aromatic phenyl carbons (3), the high binding energy shoulder at $E_B = 286.6\text{eV}$ originates from the carbon atoms (4) bonded either to the ether oxygen or the amine groups. This assignment is consistent with the intensity ratios of the bands and the calculations of Silverman et al. /7/ on aromatic amino compounds. The N 1s spectrum of this ODA deposit is shown in spectrum 2f. A single and symmetric N 1s band at $E_B = 400.5\text{eV}$ (FWHM = 1.4eV) indicates that both amino groups in the thick ODA film are in equivalent chemical environments. Our low coverage data for ODA on silver /6/ indicate, however, that the surface layer consists of undissociated and partly dissociated oxydianiline.

A co-deposited layer of ODA and PMDA (thickness $\sim 34\text{\AA}$) gives rise to the C 1s spectrum 2d. It is obvious that spectrum 2d is not simply a composite of the PMDA and ODA C 1s spectra, but a chemical reaction between the two molecules has changed the carbon 1s binding energies of the two reactants. Spectrum 2d resembles the spectrum of polyamic acid reported by Leary and Campbell /8/ which was prepared by solvent removal from a dissolved ODA film. Amister /9/ and the group of S. J. Lin et al. of VTT of

deposited polyamic acid /3/. In polyamic acid, the carbonyl carbon atoms are in a variety of acid and amide chemical environments, resulting in a broad band in the carbonyl C1s region. Since the exact stoichiometry of the co-deposited surface layer is not known, assignment of the C1s bands to specific carbon atoms is at present not possible.

The co-deposited layers ($d \sim 34\text{\AA}$) were slowly heated in vacuum and desorption of water, ODA and PMDA was observed. As shown in Fig. 3 for O1s data, the significant removal of water was achieved by heating. The O1s band of the co-deposited layer at room temperature (Fig. 3a) shows a doublet with a high binding energy band at $E_B = 534.4\text{eV}$ assigned to emission from the hydroxyl groups and the low binding energy band ($E_B = 532.7\text{eV}$) originating from the carbonyl and ether oxygen. By heating to 180°C the band narrows due to loss of hydroxyl groups as water. For annealing at temperatures greater than this the spectrum gradually changes into the one expected for the polyimide film.

The film thickness decreased continuously during heating. After 10 min. at 180°C the attenuation of the Ag 3d emission indicated a thickness of $\sim 14\text{\AA}$, and after heating to 300°C for 1 hour of $\sim 11\text{\AA}$. The resulting C1s and O1s spectra after curing at 300°C for 1 hour are displayed as Figs. 2e and 3c respectively. They are identical to those obtained by us for thick ($d > 73\text{\AA}$) polyimide films /6/ or those produced by spin coating techniques /8/. In agreement with the data and calculations by Ho and co-workers /1,2,7/ we assign the C1s band (3) at $E_B = 286.2\text{eV}$ to the aromatic carbon in the ODA part of the polyimide, the band (1,4) at $E_B = 286.9\text{eV}$ to the carbon in the PMDA ring and carbon to nitrogen or oxygen the ODA part of the polymer, and the band (2) at 290.0eV to the carbonyl carbon in the polyimide /6/. In the O1s data the peak is assigned to the carbonyl oxygen in the polyimide ($E_B = 533.4\text{eV}$) and the ether oxygen in the ODA constituent of the polyimide ($E_B = 534.9\text{ eV}$).

Integration of the carbonyl band C(2) and the C(3) and C(1,4) band gives a ratio of C(2):C(1,4):C(3) $R = (4):(9.5):(9.6)$ as compared to $R = 4:10:8$ for a stoichiometric polyimide film. The relative higher intensity of the low binding energy C1s peak at 286.2eV can be explained by the polyimide film having a high branching ratio and terminal ODA groups and/or by the presence of fragmented PMDA and ODA in the polyimide-silver interface. That fragmented PMDA and/or ODA contribute to the spectra of the thin ($\sim 11\text{\AA}$) film is also evident in the O1s spectra (Fig. 3c) by the low binding energy shoulder persisting around $E_B = 531.5\text{eV}$. This shoulder was also observed for monolayer coverages of PMDA and ODA and indicates

again fragmentation in the polyimide-silver interface.

As shown in Figs. 2f-2h, the reaction of ODA and PMDA to form the polyimide can be followed by the changes in the N1s spectra. Co-deposition leads to broadening of the N1s band (2g), indicating a reaction of the NH₂-groups with the PMDA anhydride groups. With an increasing degree of imidization, the N1s band narrows and centers at 401.5eV in the fully cured polymer (2h).

• The total C:O:N ratio in the thin polymer film is $R = (24.8):(4.9):(2)$. For a stoichiometric polymer a ratio of $R = (22):(5):(2)$ is expected. The excess carbon in our film is present as aromatic carbon, since the carbonyl carbon to total oxygen ratio is reduced to 2.9/5 as compared to 4/5 for a stoichiometric film. A carbonyl deficiency in polyimide films has been noted in previous XPS studies on polyimide surfaces, but in our very thin film a stoichiometric ratio is obtained for the total oxygen to nitrogen ratio with an excess of aromatic carbon. This observation is also consistent with a polyimide/metal interface consisting of partially fragmented PMDA and ODA where some of the carbonyl and amino groups are lost as CO and aniline during initial deposition, respectively, and is supported by our O1s data as noted earlier. The oxygen species with the lowest binding energy being identified as the oxygen bonded directly to the silver surface. We therefore conclude that adhesion of the polyimide film to the silver surface involves chemical bonding to the silver surface via fragmented PMDA and ODA.

We carried out several unsuccessful experiments to produce thinner polyimide films on silver surfaces by either co-deposition of ODA and PMDA or by evaporating the individual components sequentially. Co-deposited layers of $\sim 12\text{\AA}$ thickness initially showed photoemission spectra consistent with the presence of polyamic acid, but heating the layer led to a decrease in effective thickness and dissociation of the organic constituents in the silver-polymer interface. From the intensity of the carbonyl C1s emission from imide carbonyl groups we estimate that only $\sim 15\%$ of the polyamic acid present after initial co-deposition underwent imidization. Similar results were obtained by sequential evaporation of thin ($d \sim 5\text{-}7\text{\AA}$) ODA and PMDA layers, supporting our conclusion that the silver-polymer interface consists of fragmented and chemically bonded polymer constituents through which adhesion to the substrate is achieved.

In conclusion, our experiments show for the first time that adhesion between a polyimide film and a bulk metal surface is achieved by chemical bonding to the substrate. As demonstrated in this work, the

polyimide films can be prepared in a controlled fashion by vapour deposition techniques allowing the application of surface sensitive spectroscopies to study the chemistry and physics of adhesion, the effect of contaminants or adhesion promoters in the interface, and the chemical reactions during polymerization in ultra thin polyimide films.

Acknowledgements

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Figure Captions

Fig. 1 Schematic representation of the reaction of ODA and PMDA to form polyimide.

Fig. 2 C 1s and N 1s spectra of PMDA, ODA and their reaction products on polycrystalline silver.

2a C 1s PMDA d ~ 4Å (x 2).

2b C 1s PMDA d ~ 11Å.

2c C 1s ODA d ~ 17Å.

2d C 1s co-deposited film of ODA and PMDA, d ~ 34Å.

2e C 1s cured polyimide (1 hour 300°C), d ~ 11Å.

2f N 1s of ODA, d ~ 17Å.

2g N 1s of a co-deposited film of ODA and PMDA, d ~ 34Å.

2h N 1s of cured polyimide, d ~ 11Å.

Fig. 3 O 1s spectra of a co-deposited ODA + PMDA layer and their eventual reaction on polycrystalline silver to form polyimide.

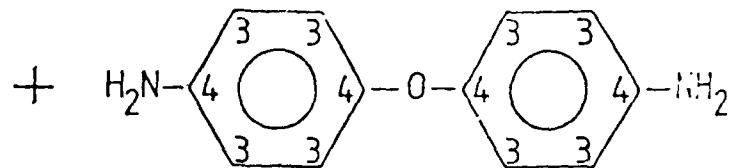
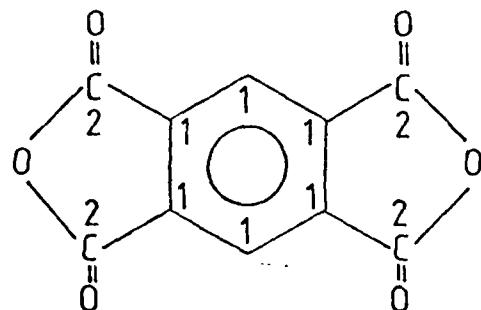
3a 36Å room temperature.

3b 14Å following heating to 180°C 10 mins.

3c 11Å further heating at 300°C 60 mins.

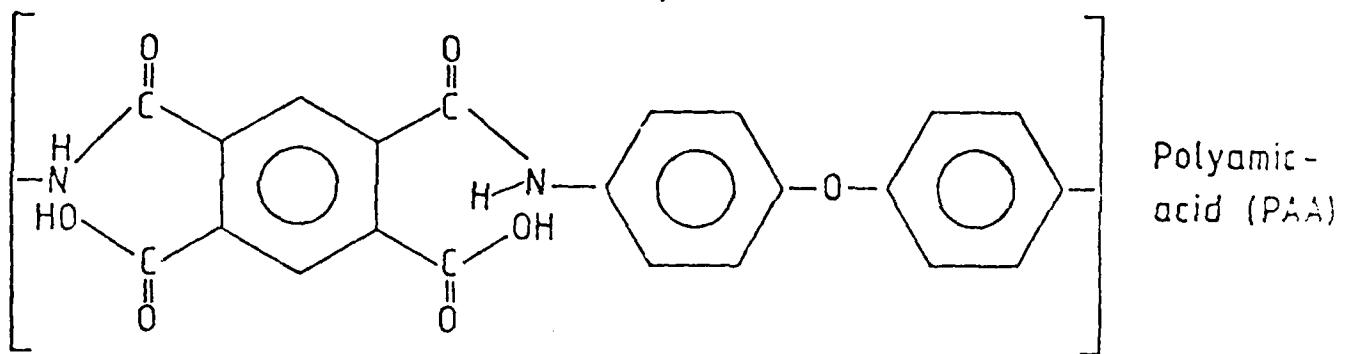
ODA + PMDA

Polyimide



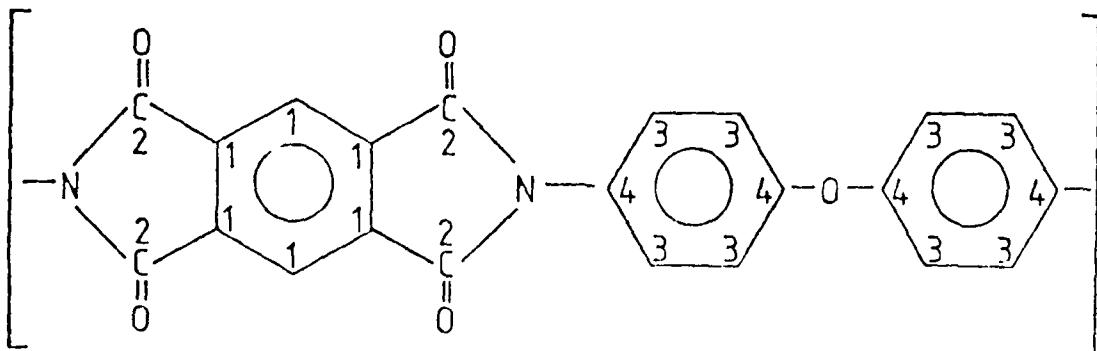
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Anhydride
PMDA

4,4' Oxydianiline
ODA

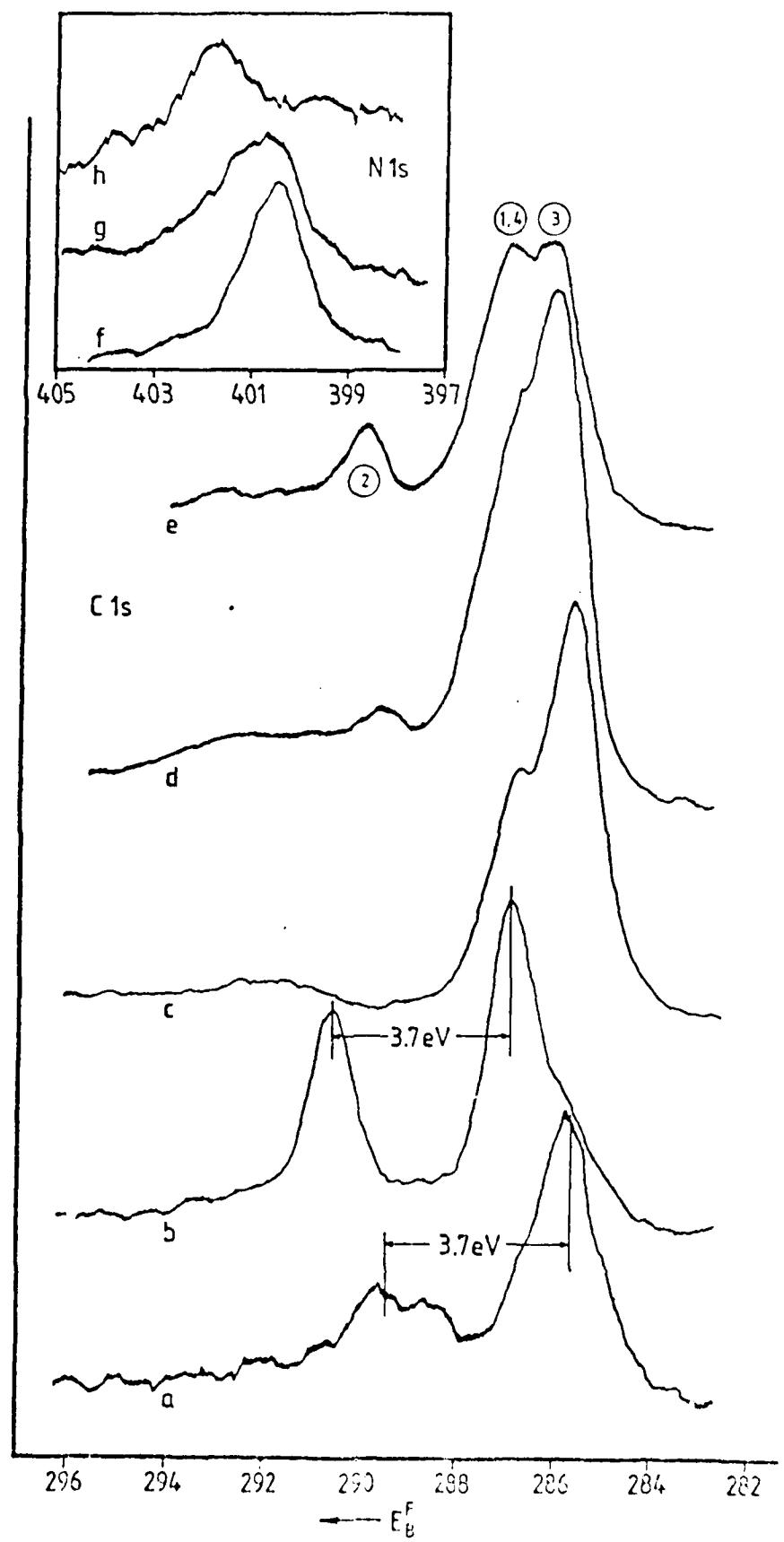


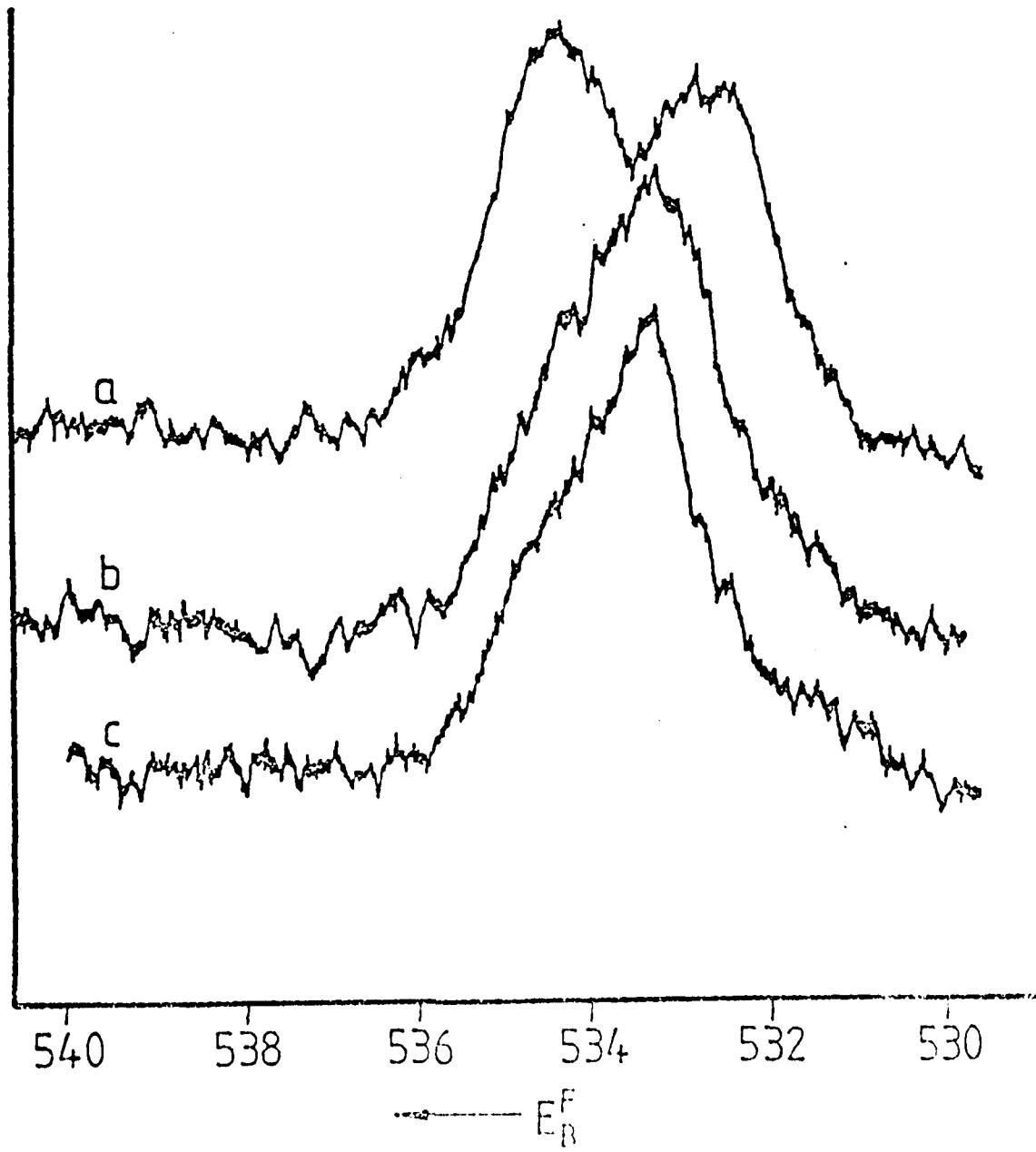
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Polyimide (PI)





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